Evidence for intervalence charge-transfer (IVCT) states in Eu-doped phosphors

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Divalent europium is one of the most studied luminescence activators, due to its huge application potential thanks to its color tunability across the visible spectral range. This is reflected in the large-scale use of Eu-based phosphors in state-of-the-art white light emitting diodes (LEDs) [1]. Despite the large efforts that have been devoted to optimize phosphors, high efficiencies are often not been reached due to loss mechanisms of which the nature is often not known, yielding suboptimal quantum efficiencies or stronger thermal quenching.

The multivalent nature of Eu is yet another challenge, as Eu^{2+} and Eu^{3+} are both stable ions in many hosts. Distributions of both activators can be expected in Eu-doped materials, which enables intervalence charge transfer (IVCT) transitions, potentially drastically affecting luminescence properties. Indeed, it was recently shown that IVCT is responsible for the anomalous emission in Ce-doped elpasolites and Yb-doped fluorides [2,3].

Here, we show direct evidence of Eu^{2+}/Eu^{3+} IVCT states in a series of representative luminescent materials: Eu-activated CaF_2, SrF_2, and BaF_2. Evidence of IVCT states in Eu-doped materials was so far missing. Independently and unanimously, state-of-the-art relativistic multiconfigurational *ab initio* embedded cluster calculations and diffuse reflection spectroscopy show that the IVCT states intercalate between the ground ($4f^7$) and the luminescent ($4f^65d$) states of Eu^{2+}. We show how the location of IVCT levels is affected by changing the chemical composition of the host compound [4].

References

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